PYROLYSIS OF NATURAL RUBBER, WAXES AND RESINS WITH ZEOLITIC CATALYSTS.

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INTRODUCTION

In recent year there has been considerable interest in developing renewable resources, as alternatives to petroleum based substances. Oil and hydrocarbon producing plants, mostly growing in arid regions, are especially promising candidates to produce important chemical intermediates and fuels. (1-4).

In previous work (5,6), we have evaluated chemically the potential of some Chilean species growing in arid lands as hydrocarbon producing crops. Among the studied species, Euphorbia lactiflua, Euphorbia copiapina, Tessaria absinthioides and Bulnesia chilensis turned out to be promising sources of polyisoprene and/or n-paraffins. Their extracts are potential starting materials for fuels and/or chemicals through pyrolytic reactions. However, it is necessary to study the effect of various catalysts on the pyrolysis and identify the most promising ones, in order to utilize economically these plants.

Most of the work on the pyrolytic reactions of biomass were carried out with the carbohydrates. (8). There is very little known on the influence of catalysts, pretreatments and other reaction conditions on the compounds obtainable through the pyrolysis of the extracts from latex producing plants. It has been reported that mixtures of ethylene, propylene, toluene, xylenes, C_5 through C_{20} nonaromatics, and C_1 to C_4 alkanes can be obtained when these extracts are pyrolyzed in the presence of ZSM-5, a molecular shape-selective zeolitic catalyst developed by Mobil Oil Corporation (7).

It is difficult to taylor-make "a priori" a catalyst for all the types of reaction that take place in converting biomass extracts to valuable chemicals. However, we theorize that owing to their acidic and structural properties, such as larger pore size and central cavity size than those of

ZSM-5, thermostable zeolitic faujasites would be appropriate. Some bi-functional catalysts, e.g. Pt/faujasite, would be also good candidates to improve reduction of carbonyl groups and to diminish the formation of coke which deactivates the catalyst.

To assess the possibility of obtaining fuels, the main components of CH_2Cl_2 extracts from Chilean species,i.e.,polyisoprene, n-paraffins and resins, were pyrolyzed with various zeolitic catalysts, utilizing different heating rates and subtrate/catalyst (S/C) ratio. Conversion degree and best conditions of pyrolysis were estimated by means of thermo-gravimetry and differential scanning calorimetry.

EXPERIMENTAL

Extraction, fractionation and analysis.

Plant species were collected from the wild, in the North of Chile (III and IV Regions). Voucher specimens were kept at the University of Concepcion Herbarium (Conc.). Samples of latex from Euphorbia lactiflua were collected by tapping wild plants.

Dried milled samples were extracted in a Soxhlet apparatus with CH_2Cl_2 for 40 hours. After the evaporation of the solvent, the solids were again extracted using acetone to obtain acetone-soluble and acetone-insoluble fractions. Representative fractions were characterized by quantitative analysis, IR, ^1H and ^{13}C NMR spectroscopy, TLC and GC (5,6). Results are given in Table 1.

Isolation and Characterization of main components.

n-Paraffins.

Acetone-insoluble fractions were refluxed in a suspension of activated carbon, Johns-Manville cellite and hexane, filtered and dried to obtain the fractions of refined hydrocarbons which were analyzed by IR, ^1H NMR, ^{13}C NMR, and GC. (5).

NMR and IR spectra of refined hydrocarbons from different species revealed almost exclusively the presence of n-paraffins. The identification of hydrocarbons was carried out by the comparison of RRt data with those of authentic standards. The results revealed the presence of n-alkanes mixtures with chain lengths varying from n-nonadecane (n-C_{19}) to n-tritriacontane (n-C_{33}). In the mixture, n-heptaeicosane (n-C_{27}), n-

nonaeicosane (n-C_{29}) and n-hentriacontane (n-C_{31}) were the dominant alkane components.

Rubber

Fresh latex from E. lactiflua was mixed with C_2Cl_4. After removing the azeotrope, the solid was dried at 50°C for 12 hours. Dry latex was dissolved in CH_2Cl_2, then filtered, and the solution was added drop by drop to methanol. The precipitate was centrifuged, dried in a vacuum oven at 50°C for 2 hours and weighed. The yield was 8.05% in dry latex weight basis. The characterization was done by IR, NMR spectroscopy (^{13}C and ^{1}H) and TLC. All the data obtained agreed with those given in literature for cis-1,4-polyisoprene.

Resins

Resins isolated through succesive fractionation of dry latex from E. lactiflua and CH_2C1_2 extract from C. odorifera were characterized by I.R., ^{13}C NMR and TLC with standards (5). The main components were: sterols (B-sitosterol-type), fatty alcohols (oley-type), fatty acids (oleic-type).

Preparation and Characterization of Catalysts

Series of HNaY, MNaY and M_1M_2NaY (M = Pt, Co, Mo) zeolites were prepared by impregnation or partial sodium exchange of a NaY zeolite faujasite-type (Linde, Si/A1 = 2.4) with NH_4^+ or suitable metalic ions. The degree of ionic exchange was determined by atomic absorption sodium analysis in the filtrate. Dehydration, deamination and dehydroxilation were carried out at 110°C, 250-420°C and 480-550° respectively. Reduction of PtNaY catalyst was carried out with H_2 at 520°C (9-10).

The crystallinity of the exchanged zeolites was determined by X-ray diffraction using the powder method (11). The specific areas of the prepared zeolites were determined by the absorption method of N_2. The analysis were performed in a volumetric BET conventional equipment at -196°C (12). The number of acid centers and their relative strengths were determined by a potentiometric method (13). Results are given in Table 2.

Thermogravimetric analysis.

C. odorifera n-paraffins, E. lactiflua polyisoprene and E. copiapina resins were selected as model substrates. The rate of weight loss, and the

weight of the residue of each substrate, catalyst, and mixtures S/C, were determined in a T.G.A. under N_2. A temperature range of 50-550°C and heating rates of 20, 40 and 80 degrees/min were used. The results for samples S/C = 1/1 (wt/wt) are given in Table 3. Percents of total weight loss (substrate + catalyst) were corrected and are given in percent of weight loss of the substrate.

DSC analysis

Calorimetric studies were carried out on a DSC-system, upon heating from 30 to 500°C at 80°C/min. The samples were sealed in aluminum pans with a pinhole on top for the escape of volatiles, which were flushed out of the reaction zone with a constant flow of N_2.

RESULTS AND DISCUSSION

According to the results of Table 3, as the heating rate increases, the T_{infl} also does. The T_{infl} is around 330 to 390°C and it is higher for the substrates without catalyst. The percent of weight loss at this point is from 37 to 64%, therefore it could be assumed that most of the pyrolytic products are formed around 400°C.

Results for samples S/C = 9/1 (wt/WT) are not given because were not reproducible. This may be due to the fact that it is very difficult to obtain homogeneous samples with this ratio, and a small error in the quantity of catalyst may cause a large error in the results.

In the DSC analysis, the pyrolysis of the mixtures S/C = 1:1 (wt/wt) could be separated into two large and broad peaks: one endothermic, with maxima around 200°C, the o ther, exothermic, with maxima around 430°C.

Below 300°C a minimal amount of volatile material is generated (Table 3), and the first range endothermic peak is probably due to melting and minor scissions. On the other hand, the second range temperature, exothermic peak, is located, within the experimental error, in the zone of maxima volatization rate (Table 3), therefore, an extensive decomposition seems to take place around 400°C.
The temperature of the maxima of the exotermic peak is lower for most of mixtures S/C than for the substrates without catalyst showing that they speed up the pyrolysis.

CONCLUSIONS

General conclusions emerging from the results are:

- The catalysts speed up the process of pyrolysis and enhances the percent of conversion of all substrates.
- The better conditions for the catalytic pyrolysis would be temperatures around 400°C and higher heating rate.
- Regarding the percentage of conversion (% wt final), the catalysts that seem to direct .more efficiently the pyrolysis of the extracts of hydrocarbon producing plants to mixtures with low C/H ratio, besides ZSM-5, were: Co(1)NaY, Mo(2)NaY and Co(1) Mo(0.5)NaY.

Continuing work.

The composition of pyrolytic volatile products and theirs combustion heats are being investigated to make the final conclusions about the most suitable pyrolytic conditions. Further results from these studies will be reported in the near future.

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TABLE 1
YIELD, MOLAR RATIO C/H OF REPRESENTATIVE FRACTIONS AND POLYMERIC HYDROCARBON TYPE FROM SOME CHILEAN SPECIES.

SPECIES	CH_2Cl_2 EXTRACT		ACETONE-INSOLUBLE FRACTION		POLYMERIC HYDROCARBON TYPE[C]
	YIELD [A]	C/H RATIO[B]	YIELD[A]	C/H RATIO[B]	
E.LACTIFLUA	10.80	0.52	2.90	0.48	NR, WAXES
E.COPIAPINA	11.70	0.57	3.10	0.51	NR[D], WAXES
C.ODORIFERA	4.50	0.54	2.20	0.48	NR[D], WAXES
C.SALICIFOLIA	5.30	0.55	1.60	0.49	NR[D], WAXES
T.ABSINTHIOIDES	7.40	0.57	1.32	0.52	WAXES

A. Given as a percentage of plant dry weight; average value of extracts from 2-3 plant samples
B. C/H molar ratio calculated from quantitative analysis data
C. NR=natural rubber (cis-1,4-polyisoprene) identified by spectroscopic data
D. Traces.

TABLE 2. CHARACTERISTICS OF THE PREPARED ZEOLITES

DEGREE OF I.E. OR IMPREGNATION	SOLID DENOMINATION	CRYSTALLINITY %	S_{BET} (M^2G^{-1})	RELATIVE ACID STRENGTH
40% NH_4	H(40)-NAY	100	726	STRONG
64% NH_4	H(64)-NAY	100	713	STRONG
0.5 Wt % Pt	Pt (0.5)-NAY	100	680	WEAK
1Wt% Co(AS CO_3O_4	Co (1)-NAY	100	722	MODERATE
2Wt% Mo(AS MoO_3)	Mo (2) NAY	85	615	MODERATE
1Wt% Co ($ASCo_5O_4$)	Co (1) Mo (0.5)-NAY	90	710	MODERATE

I.E. =Ionic exchange

TABLE 3. THERMOGRAVIMETRIC ANALYSIS FOR MIXTURES S/C=1/1 wT/WT).

n	CATALYST	HEATING RATE (DEGREE/min.	$T._{INF.}$ (°C)	$\%W.L._{INF.}$	T_F (°C)	$\%WL._F$
P	-	20	370	64.0	430	95.4
A	ZSM-5	20	350	50.6	480	91.0
R	H(40)NAY	20	320	51.8	460	93.5
A	H(64)NAY	20	330	46.6	450	92.5
F	Pt(0.5)NAY	20	315	23.9	450	68.7
F	Co(1)NAY	20	310	39.1	450	89.7
I	Mo(2)NAY	20	325	38.5	450	98.2
N	Co(1)Mo(0.5)NAY	20	320	41.8	450	94.8
S	-	40	390	55.2	480	85.9
	ZSM-5	40	360	46.2	480	84.4
	H(64)NAY	40	350	45.4	470	94.6
	Pt(0.5)NAY	40	330	24.5	460	61.8
	Co(1)NAY	40	330	37.6	450	90.8
	Mo(2)NAY	40	350	38.1	450	91.5
	Co(1)Mo(2)NAY	40	340	37.8	490	88.3
	-	80	420	53.0	490	82.9
	ZSM-5	80	390	40.0	470	89.7
	H(40)NAY	80	380	43.9	460	89.5
	H(64)NAY	80	360	46.7	480	92.2
	Mo(2)NAY	80	390	45.0	510	92.0
	-	20	350	46.1	450	82.1
R	ZSM-5	20	310	41.6	350	84.4
E	H(40)NAY	20	310	37.5	450	77.4
S	H(64)NAY	20	295	38.2	400	75.4
I	Pt(0.5)NAY	20	270	27.9	400	60.0
N	Co(1)NAY	20	300	36.9	450	75.0
S	Mo(2)NAY	20	320	48.4	450	98.4
	Co(1)Mo(0.5)NAY	20	300	43.7	400	83.6
	-	40	380	41.4	450	78.3
	ZSM-5	40	350	44.8	460	80.5
	H(40)NAY	40	330	40.9	420	81.8
	H(64)NAY	40	310	40.2	400	82.4
	Pt(0.5)NAY	40	300	34.8	450	77.0
	Co(1)NAY	40	300	43.9	450	95.2
	Mo(2)NAY	40	330	49.6	450	97.4
	Co(1)Mo(0.5)NAY	40	330	38.9	450	87.3

Continuation of TABLE 3.

CATALYST	HEATING RATE (DEGREE/min.	$T_{INF.}$ (°C)	%W. $L_{INF.}$	T_F (°C)	%WL_F
P -	20	390	42.9	460	82.9
O ZSM-5	20	385	50.0	450	91.5
L H(40)NAY	20	375	49.8	450	78.4
Y H(64)NAY	20	370	38.1	480	72.4
I Pt(0.5)NAY	20	400	36.6	470	57.4
S Co(1)NAY	20	350	31.5	450	91.9
O Mo(2)NAY	20	350	29.2	450	71.9
P Co(1)Mo(0.5)NAY	20	370	48.4	450	87.4
R					
E -	40	406	33.1	490	88.4
N ZSM-5	40	390	42.8	500	96.1
E H(40)NAY	40	390	47.3	470	88.6
H(64)NAY	40	370	40.3	480	80.8
Pt(0.5)NAY	40	340	25.3	500	75.0
Co(1)NAY	40	380	34.2	500	96.2
Mo(2)NAY	40	370	37.3	450	88.6
Co(1)MO(0.5)NAY	40	385	48.1	450	89.8
-	80	425	51.1	510	93.3
ZSM-5	80	400	46.6	500	97.7
H(40)NAY	80	390	42.5	460	86.0
H(64)NAY	80	400	39.2	480	79.4
Mo(2)NAY	80	410	45.0	510	82.1

$T_{INF.}$ = Temperature at inflection point

%WL INF. = % of weight loss at $T_{INF.}$

I_F = Temperature where no more weight loss occurs

$\%WL_F$ = % of weight loss at T_F.